AD-A051 451   PRINCETON UNIV   N J   DEPT OF CHEMICAL ENGINEERING   F/G 11/9
                THE FORMATION AND PROPERTIES OF NETWORK POLYMERIC MATERIALS.(U)
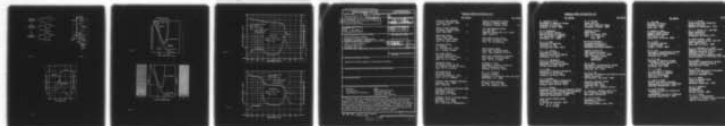   MAR 78   J K GILLHAM   N00014-76-C-0200
UNCLASSIFIED   TR-15   NL

AD
A051451

END
DATE
FILMED
4-78
DDC

OFFICE OF NAVAL RESEARCH

Contract N00014-76-C-0200

Task Number NR 356-504

TECHNICAL REPORT NO. 15

THE FORMATION AND PROPERTIES

OF NETWORK POLYMERIC MATERIALS

by

J. K. Gillham

Address Delivered in Connection with Receipt of

THE AMERICAN CHEMICAL SOCIETY AWARD

IN THE CHEMISTRY OF PLASTICS AND COATINGS,

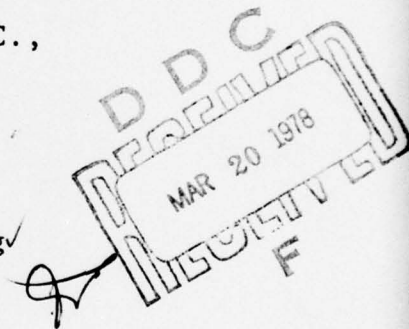Sponsored by   BORDEN FOUNDATION, INC.,

Anaheim, California, March 1978

Polymer Materials Program
Department of Chemical Engineering
Princeton University
Princeton, N. J. 08540

March 1978

J. K. Gillham
Principal Investigator
609/452-4694

THE FORMATION AND PROPERTIES
OF NETWORK POLYMERIC MATERIALS

John K. Gillham
Polymer Materials Program
Department of Chemical Engineering
Princeton University

Polymeric materials are of two types, thermoplastics and
thermosets. Unlike thermosets, thermoplastics (e.g., poly-
ethylene, polystyrene, and polyvinyl chloride) soften and flow
on heating and, when cooled, can return to their original state.
The techniques of processing them (e.g., injection molding and
extrusion) depend on this reversible behavior. Synthesis and
processing of thermoplastic materials are distinct operations.
On the other hand, thermosets are generally polymerized and
processed in a single operation (e.g., compression molding),
which transforms low molecular weight material to network poly-
mer of infinite molecular weight in an irreversible process.
Examples are epoxy and unsaturated polyester resins of fiber-
reinforced composites used in ships.

In spite of their superior engineering properties as solid
materials, thermosets have been neglected scientifically in
comparison with thermoplastics. The reason lies in their in-
tractability -- which is the very characteristic that makes them
so important. The present article shows how an experimental
examination of the phenomena encountered in their formation
leads to an unusual and yet general way of regarding both

thermoplastics and thermosets. Systematic perturbation of the model should produce fuller understanding of the parameters which bear on the molecular engineering of thermosets.

The molecules of thermoplastic materials are linear and can be synthesized from bifunctional reactants (e.g., A-B). For example, if A in one molecule reacts with B in an adjacent molecule on a one-to-one basis, n molecules of monomer A-B may polymerize to a linear molecule with a repeat unit {A-B}. Three dimensional network polymers can be synthesized from systems containing multifunctional (> 2) reactants; for example,

$$m A \underset{|}{\overset{A}{\underset{A}{\rule{2cm}{0.4pt}}}} A + 3/2 \, m \, B\text{-}B$$
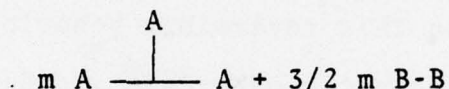
will form a network molecule. The network structure confers macroscopic dimensional stability to the thermosets which are therefore used in applications demanding high performance. Diamond, rubber, and quartz are other examples of network molecules. In contrast, thermoplastics flow under stress, which limits their uses to those in which stability under load is not so important.

Gelation and vitrification are two macroscopic phenomena which are encountered during the reaction which converts a liquid to a solid in the thermosetting process. Gelation, like a chemical explosion, is an example of a critical condition being reached in a chemical reaction. It is associated with a

dramatic increase in viscosity and a corresponding decrease in processibility that occur at a calculable degree of reaction for the particular reactive system. On the molecular level, this corresponds to the incipient formation of branched molecules of mathematically infinite molecular weight. Below the critical degree of reaction all of the molecules have finite size; at higher chemical conversions some are "infinite", their number and size increasing with chemical conversion. A network develops by intramolecular reactions of branched molecules (Figure 1). Eventually the total mass can be one molecule with a molecular weight per gram-mole of more than Avogadro's number (6×10^{23}) and limited only by the amount polymerized. The mathematical theory of gelation was formulated many years ago by Paul Flory, the recipient of the Nobel Prize for Chemistry in 1974.

Vitrification is the formation of a glassy solid. In thermosets this usually follows gelation and then occurs as a consequence of the network becoming tighter through further chemical reaction (crosslinking). A network structure will be a rubber (elastomer) at a given temperature if the segments between junction points of the network are flexible. If the segments are immobilized by further chemical reaction, or by cooling, the structure will change to a glassy (vitrified) state. Vitrification can prevent further reaction. The overall transformation from liquid to gel to rubber to glass due to chemical reaction is termed "cure".

An automated torsion pendulum has been developed which permits monitoring of the changes which occur throughout cure (1). A composite specimen is made by impregnating a glass fiber braid with a solution of the reactive system and removing the volatile solvent. After mounting the specimen, the pendulum is intermittently set into oscillation to generate a series of freely damped waves. The character of each of these waves changes throughout cure. Two mechanical functions, rigidity and damping, are obtained from the frequency and damping constants which characterize each wave. A schematic diagram of the pendulum is shown in Figure 2.

The experimental results for the cure of an epoxy system at a series of constant temperatures were used to obtain the gelation time and the vitrification time versus cure temperature. These transformation times were measured using peaks in the mechanical damping curves; they correspond to points of inflection in the rigidity curves (see Figure 3 which results from an isothermal experiment at an intermediate temperature). Results derived from a family of isothermal plots are summarized in Figure 4 which shows that there are three types of behavior depending on the temperature of cure. At high temperatures the liquid gels but does not vitrify. At low temperatures the liquid vitrifies, and need not gel if the chemical reactions are quenched by vitrification. At intermediate temperatures the liquid first gels and later vitrifies (Figure 3). The time to gelation decreases exponentially with temperature since the degree of reaction at the point of gelation is constant. In contrast, it is

noted that the time to vitrify passes through a minimum which occurs at intermediate temperatures of cure. This reflects competition between the increased rate constants for reaction and the increased degree of reaction required to overcome the thermal motions for vitrification at higher temperatures. The temperature at which gelation and vitrification occur together is defined as T_{gg} (Figure 4). Vitrification can occur before gelation ($T_{cure} < T_{gg}$) simply by an increase of molecular weight. Gelation occurs without vitrification when cure is performed above the maximum softening point, the maximum glass transition temperature $T_{g\infty}$ of the system (Figure 4). It is also apparent that if reactions cease at vitrification ($T_{cure} < T_{g\infty}$), the glass transition temperature, T_g, of the system after cure will equal the temperature of cure. The vitrification curve therefore gives the time to reach the softening temperature which the system can achieve by curing at T_{cure}. In particular, T_{gg} is the glass transition temperature of the reactive system at its point of gelation.

A diagram such as Figure 4 summarizes much of the behavior of the thermosetting process and in particular shows that it is characterized by two temperatures, T_{gg} and $T_{g\infty}$, which will vary from system to system. In contrast, amorphous thermoplastic materials are characterized only by $T_{g\infty}$ since gelation does not occur in their formation. T_{gg} and $T_{g\infty}$ are critical temperatures of a phase diagram (Figure 4), which shows the four types of materials encountered in the thermosetting process, i.e., liquid, rubber, ungelled glass, and gelled glass.

From the practical point of view, the diagram (Figure 4) explains a number of practices in the field of thermosets. Examples follow.

1) Finite versus infinite shelf-life: If the storage temperature is below T_{gg}, a reactive material will convert to a vitrified solid of low molecular weight which is stable and can be later liquified by heat and processed; above T_{gg} the stored material will have a finite shelf-life since gelation will occur before vitrification. (A gelled material does not flow.) This concept lies at the basis of a widespread technology which includes thermosetting molding compounds with latent reactivity.

2) Post-cure: If $T_{cure} < T_{g\infty}$, a reactive material will vitrify and full chemical conversion may be prevented; the material will then need to be postcured above $T_{g\infty}$ for development of optimum properties. For the manufacture of objects of finite size it is necessary to go through a two-step process because of the exothermic nature of the reactions.

3) Influence of reactants: For highly crosslinkable or rigid-chain polymeric materials $T_{g\infty}$ can be above the limits of thermal stability in which case the thermoset material need not have a measurable glass transition temperature. In contrast, if $T_{g\infty}$ is below room temperature, the polymer system will be used as an elastomer.

An understanding of the relationships between bulk proper-
ties and molecular architecture is a major goal of applied
polymer science. A project is under way (2) to pursue this
quest for thermosets using as manipulable parameters gelation,
vitrification, T_{gg}, and $T_{g\infty}$, which depend on molecular consider-
ations. This will involve juxtaposing the chemistry, character-
ization, processing, and properties of thermosetting materials.

The following example (2) pertains to polymeric glassy
crosslinked matrices containing dispersed rubber inclusions.
Rubber is incorporated in inherently brittle polymeric materials
as a way of increasing toughness.

The curing of rubber-modified-epoxy systems often involves
change from an initially homogeneous solution to a heterogeneous
multiphase morphology. Evidence is presented to show that the
process of gelation arrests the development of morphology, and
therefore that the time to gelation can be used to control me-
chanical properties. The gelation time can be varied by catalysts
and temperature.

The effect of level of catalyst on the thermomechanical
behavior (rigidity and damping versus temperature) obtained
after complete cure of a single rubber-modified system is made
evident by comparison of Figure 5 (no catalyst) and Figure 6
(with catalyst). In particular, the glass transition of the
rubbery phase is more dominant for the sample cured without
catalyst and therefore with a longer time to gelation. This
result suggests that the intensity of the rubbery transition,

which directly affects macroscopic properties, depends on the time available for the development of a two phase structure. The higher glass transition temperature of the epoxy phase for the sample cured with long gelation time also suggests more complete separation of the two phases. Optical examination of the same samples supported the conclusions in that curing without catalyst led to distinctly larger size domains of dispersed rubber than cure with catalyst. Similarly, the lower the temperature of cure the longer the gelation time and the larger the size of the rubber domains. The relationship between cure temperature, gelation time, and morphology is summarized schematically in Figure 7, which demonstrates how a single chemical composition can produce distinctly different morphologies which in turn are responsible for distinctly different macroscopic behavior.

Quenching of the development of morphological changes by the phenomenon of gelation may be explained by an abrupt decrease in diffusion of rubbery material to the growing domains of rubber which occurs in the transformation from a viscous liquid to a soft gel as infinite molecules form in the process of gelation. This is a longer range and larger scale diffusion process than that which is involved in the quenching of chemical reactions which occurs in the transformation from a rubbery state to a glassy state (vitrification) by restrictions on the more localized motions of chemically reactive parts of the molecules.

There has been much art in industrial practice with these complex systems. The present article outlines an attempt to understand and logically exploit some of the underlying phenomena.

REFERENCES

1. "A Semimicro Thermomechanical Technique for Characterizing Polymeric Materials: Torsional Braid Analysis", J. K. Gillham, American Institute of Chemical Engineers Journal, Vol. 20, No. 6, pp. 1066-1079 (1974).

2. "Characterization of Thermosetting Epoxy Systems using a Torsional Pendulum", J. K. Gillham, C. A. Glandt, and C. A. McPherson, in Chemistry and Properties of Crosslinking Polymers (Ed. S. S. Labana), Academic Press, New York, New York, pp. 491-520, 1977.

ACKNOWLEDGMENT

Figure 1. Network molecules develop from branched molecules by intramolecular reactions.

Figure 2. Automated torsion pendulum. An analog electrical signal results from using a light beam passing through a pair of polarizers one of which oscillates with the pendulum. The pendulum is aligned for linear response and initiated by a computer that also processes the damped sine waves to provide the mechanical rigidity and mechanical damping data, which are plotted on an XYY plotter (1).

Figure 3. Mechanical rigidity and mechanical damping versus time during cure of an epoxy at a constant temperature ($T_{gg} < T_{cure} < T_{g\infty}$). The first peak in the damping curve represents gelation, the second vitrification. [Rigidity = $1/P^2$, where P is the period of oscillation in seconds. Damping = Δ = natural logarithm of the ratio of consecutive amplitudes of a freely decaying wave.]

Figure 4. Time to gel and time to vitrify versus isothermal cure temperature for an epoxy system. T_{gg} and $T_{g\infty}$ are critical temperatures in the phase diagram which shows the four states of materials encountered in the thermosetting process, i.e., liquid, rubber, ungelled glass, and gelled glass.

Figure 5.   Epoxy/rubber system.   O parts per hundred catalyst.   Thermo-
mechanical behavior after cure.   Experimental details and
a summary of the transitions appear in the figure.

Figure 6.   Epoxy/rubber system.   0.5 parts per hundred catalyst.   Thermo-
mechanical behavior after cure.   Compare the intensities and
temperatures of the rubber glass transition ($_{Rubber}T_g$) and
epoxy glass transition ($_{Epoxy}T_g$) of the thermomechanical
spectra of Figures 5 and 6.

Figure 7.   Development of a two-phase rubber-modified epoxy system versus
gelation time.   As polymerization progresses rubber precipitates
in domains which grow in size with time.   Gelation is considered
to arrest the growth process.   Different morphologies therefore
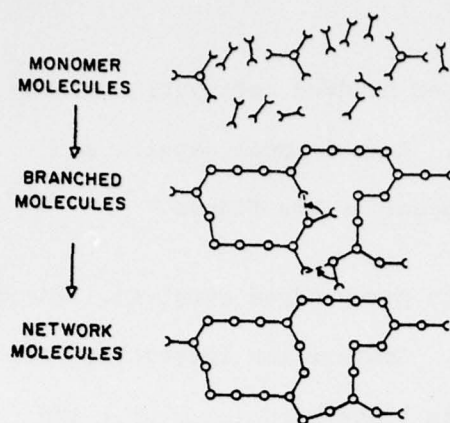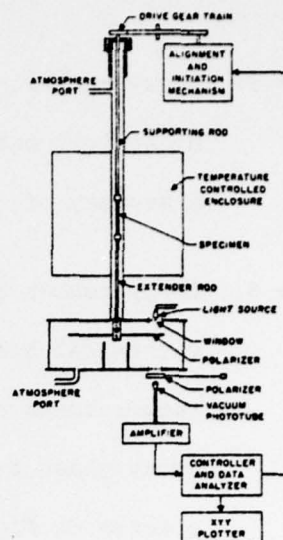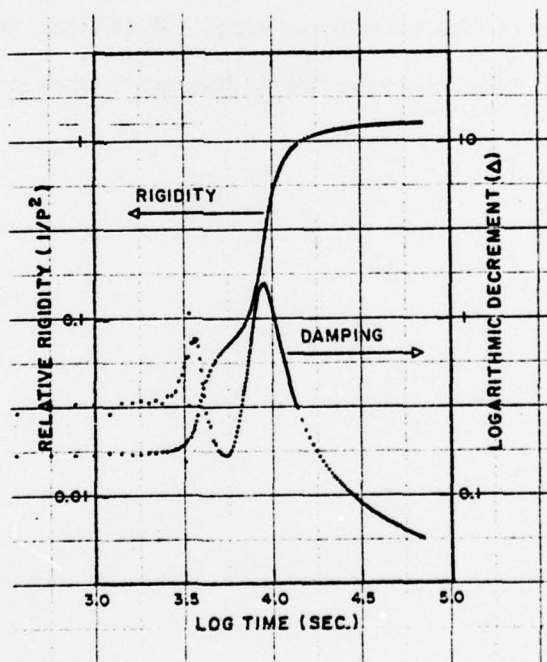result from reaction at different temperatures (e.g., T_1 and T_2).

MONOMER
MOLECULES

BRANCHED
MOLECULES

NETWORK
MOLECULES

Fig. 1

DRIVE GEAR TRAIN

ALIGNMENT
AND
INITIATION
MECHANISM

ATMOSPHERE
PORT

SUPPORTING ROD

TEMPERATURE
CONTROLLED
ENCLOSURE

SPECIMEN

EXTENDER ROD

LIGHT SOURCE

WINDOW

POLARIZER

ATMOSPHERE
PORT

POLARIZER

VACUUM
PHOTOTUBE

AMPLIFIER

CONTROLLER
AND DATA
ANALYZER

XYY
PLOTTER

Fig. 2

Fig. 3

UNGELLED GLASS

GELLED GLASS

GELATION

GLASS

TIME TO GELATION AND VITRIFICATION

VITRIFICATION

RUBBER

Fig. 4

LIQUID

GELATION

T_{gg} $T_{g\infty}$

CURE TEMPERATURE, T_{CURE}

SOLUTION

TIME →

VITRIFICATION

TIME →

SOLUTION

GELATION

T_1 T_1 T_2 T_2

CURE TEMPERATURE

Fig. 7

Fig. 5

EPOXY / RUBBER SYSTEM
0.5 % CATALYST
CURE : 170°C / 100 MIN.

PLOT : 170°C → 180°C → 170°C
ΔT/Δt = 1.5°C / MIN.
He ATMOSPHERE

TRANSITIONS

Epoxy T_g = 113°C (0.7 Hz)

Rubber T_g = −47°C (1.6 Hz)

T_{sec} ∼ −95°C

RELATIVE RIGIDITY ($1/P^2$)

LOGARITHMIC DECREMENT (Δ)

TEMPERATURE (°C)

Fig. 6

EPOXY / RUBBER SYSTEM
0% CATALYST
CURE : 170°C / 100 MIN.

PLOT : 170°C → 180°C → 170°C
ΔT/Δt = 1.5°C / MIN.
He ATMOSPHERE

TRANSITIONS

Epoxy T_g = 120°C (0.4 Hz)

Rubber T_g = −41°C (1.1 Hz)

T_{sec} ∼ −115°C

RELATIVE RIGIDITY ($1/P^2$)

LOGARITHMIC DECREMENT (Δ)

TEMPERATURE (°C)

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
Technical Report #15	TR-15	

4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED
The Formation and Properties of Network Polymeric Materials.	Technical Report. Mar 77 — Mar 78.
	6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)
J. K. Gillham	N00014-76-C-0200

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Polymer Materials Program Department of Chemical Engineering Princeton University, Princeton, N. J. 08540	Task No. NR 356-504

11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
Office of Naval Research 800 North Quincy St. Arlington, Va. 22217	Mar 78
	13. NUMBER OF PAGES
	16 p.

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report)
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release; Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Gelation	Epoxy
Vitrification	Rubber-Modified Epoxy
Transitions of Thermosets	Torsional Pendulum
	Torsional Braid Analysis

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A general model for thermosetting materials which relates polymerization to properties is discussed. In particular a phase diagram shows how the four states of matter encountered, (i.e. liquid, rubber, ungelled glass and gelled glass) relate to gelation and vitrification phenomena. The model is extended to rubber-modified thermosetting systems where evidence is presented to show, by control of the time to gelation, a given chemical formulation can provide different morphologies and hence different material behavior.

401 377

No. Copies

Office of Naval Research
Arlington, Virginia 22217
Attn: Code 472   2

Office of Naval Research
Arlington, Virginia 22217
Attn: Code 102IP   I   6

ONR Branch Office
536 S. Clark Street
Chicago, Illinois 60605
Attn: Dr. Jerry Smith   1

ONR Branch Office
715 Broadway
New York, New York 10003
Attn: Scientific Dept.   1

ONR Branch Office
1030 East Green Street
Pasadena, California 91106
Attn: Dr. R. J. Marcus   1

ONR Branch Office
760 Market Street, Rm. 447
San Francisco, California 94102
Attn: Dr. P. A. Miller   1

ONR Branch Office
495 Summer Street
Boston, Massachusetts 02210
Attn: Dr. L. H. Peebles   1

Director, Naval Research Laboratory
Washington, D.C. 20390
Attn: Code 6100   1

The Asst. Secretary of the Navy (R&D)
Department of the Navy
Room 4E736, Pentagon
Washington, D.C. 20350   1

Commander, Naval Air Systems Command
Department of the Navy
Washington, D.C. 20360
Attn: Code 310C (H. Rosenwasser) 1

No. Copies

Defense Documentation Center
Building 5, Cameron Station
Alexandria, Virginia 22314   12

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, N.C. 27709
Attn: CRD-AA-IP   1

Naval Ocean Systems Center
San Diego, California 92152
Attn: Mr. Joe McCartney   1

Naval Weapons Center
China Lake, California 93555
Attn: Head, Chemistry Division   1

Naval Civil Engineering Laboratory
Port Hueneme, California 93041
Attn: Mr. W. S. Haynes   1

Professor O. Heinz
Department of Physics & Chemistry
Naval Postgraduate School
Monterey, California 93940   1

Dr. A. L. Slafkosky
Scientific Advisor
Commandant of the Marine Corps (Code RD-1)
Washington, D.C. 20380   1

Office of Naval Research
Arlington, Virginia 22217
Attn: Dr. Richard S. Miller   1

TECHNICAL REPORT DISTRIBUTION LIST

No. Copies

No. Copie

Dr. Stephen H. Carr
Department of Materials Science
Northwestern University
Evanston, Illinois 60201   1

Dr. M. Broadhurst
Bulk Properties Section
National Bureau of Standards
U.S. Department of Commerce
Washington, D.C. 20234   2

Dr. C. H. Wang
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112   1

Dr. T. A. Litovitz
Department of Physics
Catholic University of America
Washington, D.C. 20017   1

Dr. R. V. Subramanian
Washington State University
Department of Materials Science
Pullman, Washington 99163   1

Dr. M. Shen
Department of Chemical Engineering
University of California
Berkeley, California 94720   1

Dr. V. Stannett
Department of Chemical Engineering
North Carolina State University
Raleigh, North Carolina 27607   1

Dr. D. R. Uhlmann
Department of Metallurgy and Material Science
Center for Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139   /

Naval Surface Weapons Center
White Oak
Silver Spring, Maryland 20910   1
Attn: Dr. J. M. Augl
       Dr. B. Hartman

Dr. G. Goodman
Globe Union Inc.
5757 North Green Bay Avenue
Milwaukee, Wisconsin 53201   1

Picatinny Arsenal
SMUPA-FR-M-D
Dover, New Jersey 07801
Attn: A. M. Anzalone   1
       Bldg. 3401

~~Dr. J. K. Gillham~~
~~Princeton University~~
~~Department of Chemistry~~
~~Princeton, New Jersey 08540~~   1

Douglas Aircraft Co.
3855 Lakewood Boulevard
Long Beach, California 90846
Attn: Technical Library
       C1 290/36-84
       A810-Sutton   1

Dr. E. Baer
Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106   1

Dr. K. D. Pae
Department of Mechanics and Materials Scienc
Rutgers University
New Brunswick, New Jersey 08903   1

NASA-Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135
Attn: Dr. T. T. Serofini, MS-49-1   1

Dr. Charles H. Sherman, Code TD 121
Naval Underwater Systems Center
New London, Connecticut   1

Dr. William Risen
Department of Chemistry
Brown University
Providence, Rhode Island 02912   1